

Analysis of Electrocyclic Reactions Using Localized Orbitals

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Abstract: It is pointed out that in the Woodward–Hoffmann demonstration of the concerted reactions stereospecificity (i) some energetical hypotheses concerning the transition state region are implicitly required, (ii) the MO's correlations are ambiguous if no spatial criterion is taken into account, and (iii) the demonstration itself and its application to real unsymmetric systems requires some relocation of the canonical MO's. Using a perturbative configuration interaction in a basis of localized orbitals (PCILO), one tries to analyze the energy of the transition state region. The fully localized zero-order wave function is built as an initial distorted state, a final distorted state, or a biradical state. In these three representations, the stereospecificity for a n -bond polyenic chain results from a n th order correction in the perturbation expansion representing circular delocalization effects around the reacting circle. The stereospecificity is linked directly to the parity of n without any symmetry consideration, but the energy difference between the two modes may vanish when n increases. PCILO–CNDO/2 numerical calculations for $n = 2$ support the theoretical analysis.

I. Introduction. Remarks about the Demonstration of the Woodward–Hoffmann Rules Based on Correlation Diagrams. The interpretation of the stereoselectivity of the concerted reactions¹ has been one of the great successes of quantum chemistry. In the main demonstration, the symmetry of the molecular orbitals plays the dominant role.² We would like to show that the use of symmetry orbitals for the demonstration is by no means compulsory, as already suggested by Trindle,³ and that it is even possible to give a demonstration of the stereospecificity rules using bond molecular orbital. In this demonstration the parity of the number of conjugated bonds implied in the reaction determines directly the stereospecificity.

In this first section we would like to point out three points: the Woodward–Hoffmann demonstrations require some energetical hypotheses concerning the transition state region; the correlations of MO's in these demonstrations are ambiguous if no spatial criterion is taken into account; and the demonstration itself and its application to real, unsymmetric systems requires some relocation of the MO's.

Implicit Energetical Hypothesis. The classical demonstration of the Woodward–Hoffmann rules is based on a correspondence between MO's of the same symmetry (with respect to the symmetry elements which may be kept along the reaction); the correlation occurs between the lowest energy MO of a given symmetry in the initial state and the lowest energy MO of the same symmetry in the final state; then the same operation is repeated on the second ones, and so on. This requires a qualitative positioning of the MO's energies which is very clear for the small system, because they imply σ and π MO's of very different energies, but which would be less convincing for large conjugated molecules. Then, one introduces the correlation diagrams between

states. At this stage one supposes that the energy of a determinant varies in a *regular (almost linear) way* between the energies of the extreme corresponding states. Otherwise a direct correlation between two ground state determinants does not exclude an important energy barrier.

A process which appears forbidden when one supposes a regular variation could be allowed if the determinant energies vary in a nonlinear way as the reactions takes place (Figure 1). Then, the interaction is introduced between the corresponding determinants.

Some authors have questioned the use of the non-crossing rules⁴ in the correlation diagrams but it is not absolutely necessary for the demonstration that the interaction matrix element is different from zero. If it was zero the "forbidden" processes would be even more unfavored than when one introduces the non-crossing rule.

But to get again some qualitative conclusions, one may suppose that the interaction element between the determinants is smaller than the energy differences between them. Therefore, the demonstration based on the correlation diagrams supposes (1) a regular variation of the determinants energies along the reaction, and (2) the weakness of the interaction terms between the determinants with respect to their energy differences.

It would seem worthwhile to get a direct estimate of the sign and perhaps the order of magnitude of the energy differences between reasonable transition states for the various stereochemical processes. The demonstration given in sections II–IV tries to work in that direction.

Ambiguities in the Correlation of the MO's. The correlation is in principle simply based on the symmetry and energetic characters of the molecular orbitals. Such a correlation sometimes introduces a correspondence between molecular orbitals of the initial and final states which are not defined on common atomic orbitals, *i.e.*, which are topologically completely exclusive. One may find an example of such a correlation in the butadiene–ethylene 4 + 2 Diels–Alder reaction. As al-

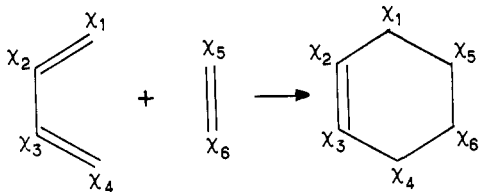
(1) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2846, 4319 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie Weinheim/Bergstr., Germany, 1970.

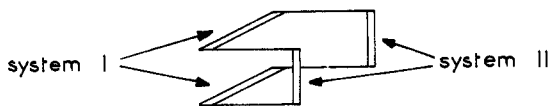
(3) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 4054 (1969); **92**, 3251, 3255 (1970); *Theor. Chim. Acta*, **18**, 261 (1970).

(4) G. Feler, *ibid.*, **12**, 412 (1968).

readily noticed by Millié,⁵ the π MO of the ethylene, defined on the $\chi_5\chi_6$ AO's, corresponds to the ethylenic orbital of the final product, defined on the $\chi_2\chi_3$ AO's.



One cannot ignore completely the topological aspect and the spatial definition of the MO's. A correlation diagram which only takes into account the symmetry and energy properties, irrespective of their localization, leads to absurd results. Woodward and Hoffmann give such an example for the *a priori* conceivable transformation of the cyclooctatetraene into a cubane molecule (ref 2, p 32). The reaction would be the sum of two cyclizations between two ethylenic systems almost orthogonal to each other. These reactions are forbidden, and the reaction cannot take place. However, the correlation rules applied without consideration of any spatial problem describe the reaction as thermally possible; this is due to the fact that the correlation occurs between MO's of the two systems.



Woodward and Hoffmann are therefore compelled to introduce a supplementary rule: "each basic process must be isolated and analyzed separately." They explain that "in fact whether a reaction is symmetry allowed or symmetry forbidden is determined by the height of the electronic hill that a reactant or product orbitals must climb in reaching the transition state. And the presence or absence of a hill is a function of the *intended* correlation, or the initial slope of the levels." By such sentences the authors introduce topological criteria, as they do when building the correct correlation diagram (ref 2, p 33), for this reaction.

A question then arises. Is it necessary to take systematically into account this spatial criterion in the correlation diagram? Why do Woodward and Hoffmann neglect this "intended correlation" in the Diels-Alder 4 + 2 reaction?⁶ When, and to what extent, is it necessary to introduce the spatial character of the MO's?

These contradictions or uncertainties will disappear completely when we work with localized MO's and the artifact of the cyclooctatetraene \rightarrow cubane reaction will not occur.

Use of Symmetry Orbitals for Substituted Molecules and the Status of the Molecular Orbitals Used. Woodward and Hoffmann say at the beginning of their review⁷ that "the semilocalized molecular orbitals," *i.e.*, the bond molecular orbitals built from two atomic or-

(5) P. Millié, *Bull. Soc. Chim. Fr.*, 4031 (1966).

(6) Reference 2, p 23. The correct correlation should occur between the π orbital of the ethylene molecule and the antisymmetrical σ^* orbital of the cyclobutene, but the error is not important for the thermal reaction, nor for the photochemical reaction from the excited butadiene. It might be important for a reaction between the ethylene excited molecule and the butadiene ground state.

(7) Reference 2, p 4.

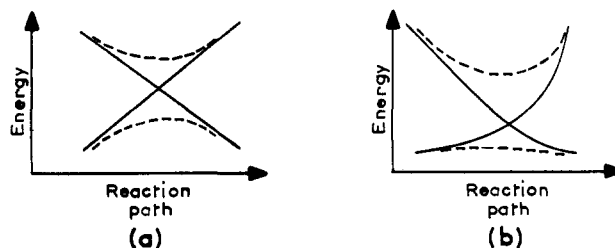


Figure 1. Illustration of the role of the regular variation of the determinant energies. (a) Linear variation of the energy; the process appears forbidden. (b) Nonlinear variation of the energy; the process is not forbidden.

bitals, properly hybridized if necessary, "are not the proper molecular orbitals. The latter are completely delocalized, subject to the full symmetry of the molecule."

One may remark immediately that they do not follow this statement, even in the simplest examples; their σ molecular orbitals used in the correlation diagrams are never "completely delocalized" as they should be to be "proper." For instance, in the Diels-Alder 4 + 2 cycloaddition of ethylene and butadiene molecules (ref 2, p 23), the σ orbitals of the cyclohexane are not really delocalized. The diagonalization of any Hamiltonian for this molecule would lead to symmetrical and antisymmetrical molecular orbitals equally spread over the whole skeleton. With such MO's, even the σ - π separation in the cyclohexene would require some relocation.

In fact, the proposed treatment is not incorrect from that point of view at least, but to support it, one must leave completely the idea that there is a unique set of proper orbitals. It is (well) known, for 20 years,⁸ that for a given n -electron determinant, there exists an infinity of equivalent sets of molecular orbitals which are obtained from each other by unitary transformations, keeping the determinant unchanged.

Then from a set of delocalized molecular orbitals, one may build equivalent sets of bond molecular orbitals, well localized on the chemical bonds. Various criteria, both intrinsic^{8b,9} and extrinsic,¹⁰ have been proposed to localize the molecular orbitals, and they all give a description of the molecule in complete agreement with the Lewis representation.¹¹

(8) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 114 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1950); **205**, 367 (1951); G. G. Hall, *ibid.*, **202**, 166 (1950); **213**, 102 (1952); (b) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, 597 (1963); *Rev. Mod. Phys.*, **35**, 457 (1963); (c) T. L. Gilbert, "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 405. This fundamental point does not appear in recently published text books in quantum chemistry. For a pedagogical review on this question see G. Berthier, "Aspects de la Chimie Quantique Contemporaine" (Colloques Internationaux du CNRS, 195), R. Daudel and A. Pullman, Ed., Centre national de la Recherche scientifique, Paris, 1971.

(9) (a) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 300 (1960); (b) S. F. Boys, "Quantum Theory of Atoms, Molecules, and the Solid States," P. O. Löwdin, Ed., Academic Press, New York, N. Y., 1966.

(10) V. Magnasco and A. Perico, *J. Chem. Phys.*, **47**, 971 (1967).

(11) For examples of *ab initio* calculations, see (a) ref 10; (b) U. Kaldor, *ibid.*, **46**, 1981 (1967); (c) S. Rothenberg, *ibid.*, **51**, 3389 (1969); (d) E. Switkes, R. M. Stevens, W. N. Lipscomb, and N. D. Newton, *ibid.*, **51**, 2085 (1969); E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3837, 3847 (1970); M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970); for semiempirical calculations one may quote, for instance, (e) C. Trindle and O. Sinanoğlu, *ibid.*, **49**, 65 (1968); (f) R. Polak, *Collect. Czech. Chem. Commun.*, **33**, 2765 (1968); (g) S. Diner, J. P. Malrieu, F. Jordan, and P. Claverie, *Theor. Chim. Acta*, **18**, 86 (1970).

Besides these delocalized and localized sets of MO's, one may imagine intermediate or partial localizations. These descriptions are as valid as the previous ones. Such an example may be found in the classical description of the conjugated systems with π delocalized and σ localized MO's. The traditional presentation of this description, which spoke of σ intrinsically localized and π intrinsically delocalized electrons,¹² is erroneous since one knows now that the π and σ MO's are practically localizable to the same extent,^{11e} but this frequent π description was by itself perfectly correct, since one may localize the σ MO's and let the π MO's delocalized.¹³

The Woodward-Hoffmann MO's represent another intermediate model where the π MO's have been localized on the π atomic orbitals (which does not appear immediately when the molecule is not planar), but where they spread in principle on the whole π system, and where the σ MO's are semi-localized, *i.e.*, delocalized on a small number of chemical bonds (*cf.* the 4 + 2 Diels-Alder reaction). Thus a partial localization is necessary even in the simplest cases considered in the theoretical demonstration.

A more important localization is necessary when one considers unsymmetrically substituted compounds. Several authors point out that "while the familiar analysis dealt with systems for which symmetry allowed an easy construction of the necessary correlation diagrams, most experimental tests involved systems without useful symmetry."³ This is the reason why Trindle, for instance, introduces nodal criteria to correlate the molecular orbitals, which represents a generalization of symmetry arguments suitable for the study of the reactions of any unsymmetrical, substituted system.³ In fact the use of symmetrical orbitals for unsymmetrical compounds is correct if one performs a localization of the molecular orbitals of this molecule on the basic symmetrical system. Let us consider, for instance, 1-methylbutadiene. In this molecule, the three delocalized π MO's obtained by diagonalization of a one-electron Hamiltonian look completely different from the butadiene MO's, each of them having an important weight on the "CH₃" system (86, 9, and 5%), but the same determinant may be written with CH bond molecular orbitals and two π delocalized MO's which are very close to the butadiene π MO's, having only a 1% weight on the CH bonds. To work with the butadiene MO's for the study of the reaction of a substituted butadiene is not so odd as it would appear when looking to the fully delocalized MO's of the substituted molecule.

What is true for hyperconjugation is true for a real conjugation. In the butadiene molecule one may find two ethylene-like localized π MO's, and if the butadiene molecule enters the reaction by only one double bond, as in the concerted $\pi_4s + \pi_2s$ Diels-Alder cycloaddition of butadiene to itself (*ref* 2, p 145), it is not necessary to make another demonstration than for the butadiene + ethylene reaction using two systems of butadiene

(12) See for instance the basic books on π electron methods.

(13) The equivalent MO's are only equivalent for the properties of a given electronic state. The symmetry delocalized MO's are necessary to represent an ionization or an excitation as a one-electron event, *i.e.*, to represent two states with two determinants using the same set of MO's. As the main success and main effort of quantum chemistry have, during a long period of time, been the interpretation of ($\pi \rightarrow \pi^*$) spectroscopy, the delocalized π MO's have been considered as the "true" MO's. This is nothing but an historical accident.

molecular orbitals (as long as the secondary effects are not involved, but for these too, the localization is worthwhile as will be demonstrated later on). In the same way, in the hexatriene molecule one may find, by an intermediate localization, one π localized MO φ_1' centered on one side of the molecule, and two π delocalized MO's φ_2' and φ_3' which resemble very closely the π MO's of the butadiene molecule. Let us call φ_1 the classical ethylenic MO and φ_2 and φ_3 the π delocalized SCF-MO's of the butadiene molecule. We have performed the calculation of the scalar products (overlaps) between the hexatriene π SCF-MO's resulting from an intermediate localization and the ethylene and butadiene π SCF-MO's. These scalar products are almost equal to unity: $\langle \varphi_1' | \varphi_1 \rangle = 0.994$, $\langle \varphi_2' | \varphi_2 \rangle = 0.996$, $\langle \varphi_3' | \varphi_3 \rangle = 0.996$. Therefore, if the hexatriene molecule acts by two double bonds as the butadiene molecule, it is not necessary to build special correlation diagrams using the three π delocalized MO's of the hexatriene molecule, to explain in a complicated way, the stereochemistry of the reaction. The demonstration already done for the butadiene molecule is still valid for hexatriene, as long as the π terminal bond is not destroyed along the reaction.

This is the reason why one may apply directly the Woodward-Hoffmann rules, demonstrated on very small systems, to very large conjugated systems. For instance it would be tedious to build a correlation diagram for the transformation of *cis*- and *trans*-benzocyclobutene (*ref* 2, p 50) and for the Diels-Alder reaction which follows and which involves 20 π electrons on a giant π system. In fact this π system may be described as two benzenic systems and two *cis*-butadiene systems with small tails of the MO's of one system on the other system. The reaction is therefore a 4 + 2 Diels-Alder reaction.

Most of the applications of the Woodward-Hoffmann rules are relevant if and only if one carries out a preliminary relocalization of the delocalized MO's inside and outside the reaction cycle itself. But one must leave then any dogmatic point of view about the "quality" of the MO's.

Then a question arises; since symmetry and localized MO's are equivalent, is it possible to perform an analysis or a demonstration of the Woodward-Hoffmann rules using localized molecular orbitals? Several types of localized MO's may be considered, among which one may distinguish between localized SCF-MO's obtained by unitary transform from the canonical SCF-MO's, and fully localized MO's. The localized SCF-MO's are mainly defined on one bond but they have small "tails" on the other bonds. These tails may be significant, and, for instance, the tails may be of different orders of magnitude in the two modes of a concerted reaction. Our method will be different; we shall start from fully localized MO's each of them being completely localized on a given chemical bond. These MO's are no longer self-consistent, and they do not satisfy the Brillouin's theorem. A lot of calculations have shown now¹⁴ that the determinant built

(14) (a) R. McWeeny and K. Ohno, *Proc. Roy. Soc., Ser. A*, **255**, 367 (1960); A. Tsuchida and K. Ohno, *J. Chem. Phys.*, **39**, 600 (1963); R. McWeeny and G. Del Re, *Theor. Chim. Acta*, **10**, 13 (1968); (b) J. D. Petke and J. L. Whitten, *J. Chem. Phys.*, **51**, 3166 (1969); (c) J. R. Hoyland, *J. Amer. Chem. Soc.*, **90**, 2227 (1968); *J. Chem. Phys.*, **50**, 473 (1969); (d) A. Masson, B. Levy, and J. P. Malrieu, *Theor. Chim. Acta*,

from these MO's is a good enough approximation to the exact wave function to be considered as the zero-order approximation of a perturbative process. The delocalization of the fully localized MO's toward SCF-MO's is obtained by a perturbation procedure which gives small tails on the neighboring bonds.

Therefore we want to start from a zero-order description of the molecule which uses typical MO's independent of the considered mode, and we shall try to analyze the origin of the stereospecificity in terms of interaction processes.

II. Localized Demonstration of the Stereospecificity for the Butadiene-Cyclobutene Reaction. (1) Method.

One attempts to evaluate directly the energy of intermediate states between the final and initial states, giving a likely representation of the transition state. In an effective calculation, one may attempt to follow the energy variation along a reaction path, or to draw the potential map for several variations of the nuclei positions. The qualitative demonstration of the stereospecificity rule is based on a direct approach of the energy in the intermediate configurations.

We attribute to the transition state an intermediate geometry between the initial state and the final state geometries. For instance, one may suppose that each bond angle and each bond length have been subjected to half of the total change when going from the initial to the final state.

The intermediate states energy is calculated by a configurational interaction between determinants built with the use of a localized molecular orbital set. The calculation method we employ is the PCILO method recently conceived^{14e} and widely used for conformational problems studies.¹⁵ The calculation process can be summarized as follows.

For every nuclear configuration (i) one builds a set of likely bond molecular orbitals both bonding (φ_i) and antibonding (φ_i^*), each of them defined on one or two properly hybridized atomic orbitals; (ii) The bonding orbitals are used to build a fully localized determinant. This determinant represents the zero-order wave function Φ_0 for the given geometry.

(iii) With the antibonding orbitals, one may build mono or diexcited determinants (or configurations). These configurations interact with the Φ_0 wave function, and the interaction between these configurations represents the configuration interaction matrix.

(iv) The ground state energy of the system will be obtained as the lowest eigenvalue of this matrix found by a Rayleigh-Schrödinger perturbation development. This mathematical process physically means that one considers the interaction between the zero-order state and the others configurations Φ_I as a perturbation. One may use indifferently for the unperturbed Hamiltonian, the Moller-Plesset or Epstein-Nesbet definitions.¹⁶

18, 193 (1970); (e) in the semiempirical framework, the PCILO method, S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta*, **13**, 1, 18 (1969); S. Diner, J. P. Malrieu, F. Jordan, and M. Gilbert, *ibid.*, **15**, 100 (1969); F. Jordan, M. Gilbert, J. P. Malrieu, and U. Pincelli, *ibid.*, **15**, 211 (1969).

(15) See for instance, B. Maigret, B. Pullman, and J. Caillet, *Biochem. Biophys. Res.*, **40**, 808 (1970); J. Langlet, B. Pullman, and H. Berthod, *J. Chim. Phys., Physicochim. Biol.*, **67**, 480 (1970).

(16) C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1964); P. S. Epstein, *ibid.*, **28**, 695 (1926); R. K. Nesbet, *Proc. Roy. Soc., Ser. A*, **230**, 312, 322 (1955).

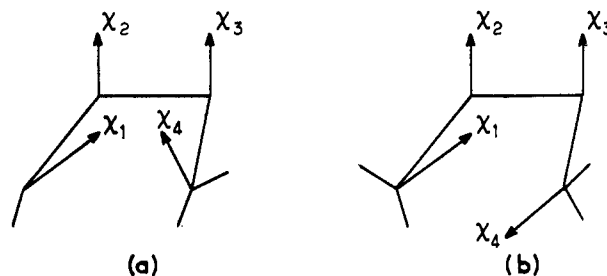


Figure 2. Definition of the atomic orbitals for the intermediate states in the reaction butadiene \rightarrow cyclobutene. The arrows represent the orientation of the atomic orbitals orthogonal to the hybrids of the invariant bonds. Their direction defines the positive lobe which is then the large one: (a) denotes the disrotatory mode, (b) the conrotatory mode.

One can represent the electronic zero-order wave function with only one determinant. In the course of the reaction, some molecular orbitals of the initial state undergo only quantitative transformations (for instance the σ bonds in the cyclizations of linear polyenes). One will call these bonds "invariant bonds."¹⁷ One will build these bonds by a criterion such as the maximum overlap¹⁸ between two atomic hybrid orbitals. In the minimal basis set at least, this procedure defines some atomic orbitals, one on each carbon atom of the cycle, which are orthogonal to the hybrids of the same center entering the invariant bonds. The reacting (or π) bonds will be defined on these AO's. For instance, in the butadiene-cyclobutene reaction, one gets four atomic orbitals orthogonal to the three σ hybrids of the same center; two of them (on the central carbon atoms) are pure π atomic orbitals, while the two others (on the external carbon) have an intermediate hybridization between pure π (p_z) and sp^3 (Figure 2).

For the electrocyclic reaction involving the n double bonds of a polyene, one gets thus $2n$ atomic orbitals χ_i orthogonal to the hybrids of the invariant bonds. With these $2n$ atomic orbitals one has to build $2n$ bonding molecular spin orbitals in order to obtain the zero-order determinant. If one calls φ' the invariant molecular orbitals and φ the reacting molecular orbitals constructed on the $2n$ atomic orbitals χ_i , the approximate ground-state determinant Φ_0 has the following form.

$$\Phi_0 = |\varphi_1' \bar{\varphi}_1' \dots \varphi_p' \bar{\varphi}_p' \dots \varphi_1 \dots \varphi_{2n}| \quad (1)$$

We can consider three sets of localized MO's φ , representing three extreme descriptions of the transition state.

(i) **Distorted Initial State.** The molecular orbitals φ are defined on the AO's χ_i in the same way as in the initial state. So in the butadiene-cyclobutene reaction, the molecular orbitals will be in the disrotatory mode

$$\begin{aligned} \varphi_1 &= (\chi_1 + \chi_2)/\sqrt{2} \text{ and } \bar{\varphi}_1 \\ \varphi_2 &= (\chi_3 + \chi_4)/\sqrt{2} \text{ and } \bar{\varphi}_2 \end{aligned} \quad (2)$$

if the orientation of the AO's χ_i is chosen according to the Figure 2.¹⁹ In the conrotatory mode, φ_2 is changed

(17) These "invariant" bonds may be some π bonds which are not destroyed in the cyclization process.

(18) G. Del Re, *Theor. Chim. Acta*, **1**, 188 (1963).

(19) It is evident from the principles of quantum mechanics, that the results are independent on the choice of the phase (*i.e.*, sign) of the MO's and AO's, but this sign must be kept constant on a given calculation.

into

$$\varphi_2 = (\chi_3 - \chi_4)/\sqrt{2} \quad (2')$$

The corresponding antibonding molecular orbitals are built on the same pair of atomic orbitals

$$\begin{aligned} \varphi_1^* &= (-\chi_1 + \chi_2)/\sqrt{2} \\ \varphi_2^* &= -(\chi_3 \pm \chi_4)/\sqrt{2} \end{aligned} \quad (3)$$

depending on the disrotatory or the conrotatory character of the cyclization. These MO's are orthogonal in the CNDO approximations.²⁰

(ii) **Distorted Final State.** We have for the molecular bonding orbitals φ a π bond between χ_2 and χ_3 and a partially broken σ bond between χ_1 and χ_4 (in the two modes)

$$\begin{aligned} \varphi_1 &= (\chi_2 + \chi_3)/\sqrt{2} \\ \varphi_2 &= (\chi_1 + \chi_4)/\sqrt{2} \end{aligned} \quad (4)$$

There are two corresponding π and σ antibonding orbitals.

(iii) **Intermediate Biradical State.** With a π bond and two unpaired electrons

$$\Phi_0 = |\varphi_1' \dots \bar{\varphi}_p' \varphi_1 \bar{\varphi}_1 (\chi_3 \bar{\chi}_4 \pm \chi_4 \bar{\chi}_3)| \quad (5)$$

Φ_0 will be a singlet or a triplet state. The φ_1 orbital represents the cyclobutane π orbital

$$\varphi_1 = (\chi_2 + \chi_3)/\sqrt{2} \quad (6)$$

It is observed that one may consider such intermediate states representations for all electrocyclic reactions whatever the number of conjugated bonds.

(2) **Ground-State Determinant Energy.** The electronic energy of the ground-state determinant Φ_0 is given by

$$E_0^e = \langle \Phi_0 | H | \Phi_0 \rangle = \sum_i \langle \varphi_i | -\nabla^2/2 + T | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) \quad (7)$$

where T represents the nuclear attraction operator and where the summations on i and j are carried over the molecular orbitals occupied in Φ_0 . J_{ij} and K_{ij} are the well-known coulombic and exchange integrals.

One adds the nuclear repulsion energy E_n to the electronic energy, E_0^e , and one gets the total energy

$$E_0 = E_0^e + E_n \quad (8)$$

It will be arbitrarily supposed here, and numerically verified in the next section, that the E_0 energy is practically the same for the two modes at the same stage of the geometrical transformation.

The E_0 energy physically represents the electrostatic interaction energy and the short distances repulsion. As the hydrocarbons bonds are not very polar, our hypothesis is equivalent to assuming that the steric repulsions are almost equal in analogous intermediate states in the two modes.

(3) **Energetic Corrections.** (a) **Distorted Initial State Representation.** The bond polarization corrections, arising from the interaction between Φ_0 and $\Phi_{i \rightarrow i^*}$, may be neglected in weakly polar molecules. For polar molecules, the interaction term $\langle i | F | i^* \rangle$ where F

is the Hartree-Fock operator relative to Φ_0 mainly depends on the bond i itself and cannot depend significantly on the considered mode.

On the contrary, one will have important delocalization corrections coming from the $\varphi_i \rightarrow \varphi_{j^*}$ monoexcitations, *i.e.*, from the electron jumps from one bond to the antibonding orbitals of the other bonds. This excitation introduces the following corrections

$$E^2_{\text{delo}} = \sum_i \sum_{j \neq i} 2 \langle \Phi_0 | H | \Phi_{i \rightarrow j^*} \rangle^2 / (E_0 - E(i^{j^*})) \quad (9)$$

where

$$\Phi_{i \rightarrow j^*} = |\dots \bar{\varphi}_{(i-1)} \varphi_j \bar{\varphi}_i \dots \bar{\varphi}_n|$$

In the CNDO hypotheses,²⁰ due to the total localization of the molecular orbitals

$$\langle \Phi_0 | H | \Phi_{i \rightarrow j^*} \rangle = \langle \varphi_i | h | \varphi_{j^*} \rangle \quad (10)$$

where h is the (kinetic energy plus nuclear attraction) mono-electronic operator.

If χ_{i1} and χ_{i2} are the two hybrid atomic orbitals entering in the fully localized bond φ_i , *i.e.*, if

$$\varphi_i = C_{i1} \chi_{i1} + C_{i2} \chi_{i2} \quad (11)$$

$$\varphi_{j^*} = -C_{j2} \chi_{j1} + C_{j1} \chi_{j2}$$

$$\begin{aligned} \langle \varphi_i | h | \varphi_{j^*} \rangle &= -C_{i1} C_{j2} \langle \chi_{i1} | h | \chi_{j1} \rangle + \\ &C_{i1} C_{j1} \langle \chi_{i1} | h | \chi_{j2} \rangle - C_{i2} C_{j2} \langle \chi_{i2} | h | \chi_{j1} \rangle + \\ &C_{i2} C_{j1} \langle \chi_{i2} | h | \chi_{j2} \rangle \end{aligned} \quad (12)$$

This formula shows that the two cyclization modes present a qualitative difference in the charge transfer $\pi \rightarrow \pi^*$ correction if we start, for example, from the distorted initial state (representation 1).

Effectively for the butadiene in the disrotatory mode

$$\langle \varphi_1 | h | \varphi_2^* \rangle = \frac{1}{2} (-\langle \chi_1 | h | \chi_3 \rangle - \langle \chi_2 | h | \chi_3 \rangle + \langle \chi_1 | h | \chi_4 \rangle + \langle \chi_2 | h | \chi_4 \rangle)$$

and in the conrotatory mode

$$= \frac{1}{2} (\langle \chi_1 | h | \chi_3 \rangle + \langle \chi_2 | h | \chi_3 \rangle + \langle \chi_1 | h | \chi_4 \rangle + \langle \chi_2 | h | \chi_4 \rangle) \quad (13)$$

From Figure 1 it immediately appears that $\langle \chi_1 | h | \chi_3 \rangle = \pm \langle \chi_2 | h | \chi_4 \rangle$ according to the disrotatory or conrotatory character of the cyclization; it follows that in the disrotatory mode

$$\langle \varphi_1 | h | \varphi_2^* \rangle = (-\langle \chi_2 | h | \chi_3 \rangle + \langle \chi_1 | h | \chi_4 \rangle) / 2$$

and in the conrotatory mode

$$= (\langle \chi_2 | h | \chi_3 \rangle + \langle \chi_1 | h | \chi_4 \rangle) / 2 \quad (14)$$

The main question concerns the signs of $\langle \chi_2 | h | \chi_3 \rangle$ and $\langle \chi_1 | h | \chi_4 \rangle$ in the two modes. With a Wolfsberg-Helmoltz-like approximation (as in the CNDO hypothesis)²⁰

$$\langle \chi_i | h | \chi_j \rangle = \langle \chi_i | \chi_j \rangle (\beta^0_i + \beta^0_j) / 2 \quad (15)$$

where β^0_i and β^0_j are two negative parameters characteristic of the atomic orbitals χ_i and χ_j . It appears immediately that the overlap $\langle \chi_2 | \chi_3 \rangle$ is always positive in two modes, while $\langle \chi_1 | \chi_4 \rangle$ is positive as soon as the reaction has progressed sufficiently in the conrotatory mode, as is apparent from Figure 3, and always positive in the disrotatory mode.

(20) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

Thus in the transition state region for the disrotatory mode, the integrals $\langle \chi_2 | h | \chi_3 \rangle$ and $\langle \chi_1 | h | \chi_4 \rangle$ are subtracted one from the other in the integral $\langle \varphi_1 | h | \varphi_2^* \rangle$ while they are added in the conrotatory mode. The delocalization contribution correction will be therefore much more important in the conrotatory mode than in the disrotatory one. It is difficult to show qualitatively that there is no important difference between the delocalization corrections $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ of the two modes. But this has been numerically checked below.

The other second-order corrections result from the interaction of Φ_0 with "diexcited" determinants giving the so-called "correlation" corrections. In the PC-ILO-CNDO hypotheses, these corrections belong to two types: on one hand, the intrabond corrections, which are bond characteristics and, therefore, in a first approximation, independent from the mode (for a more explicit verification, see ref 14e, the expression of the corresponding correction); on the other hand, the interbond correlation arising from the interaction of Φ_0 with the diexcited states

$$\begin{pmatrix} i^* & j^* \\ i & j \end{pmatrix}$$

which gives the following energetic corrections

$$4\langle ij | i^* j^* \rangle^2 / \left(E_0 - E \begin{pmatrix} i^* & j^* \\ i & j \end{pmatrix} \right) \quad (16)$$

where

$$\langle ij | i^* j^* \rangle = C_{i1} C_{i2} C_{j1} C_{j2} (g_{i1j1} - g_{i1j2} - g_{i2j1} + g_{i2j2})$$

with

$$g_{i1j1} = \langle \chi_{i1} \chi_{j1} | 1/r_{1,2} | \chi_{i1} \chi_{j1} \rangle$$

These bielectronic integrals do not depend on the orientation of the atomic orbitals. In the CNDO hypothesis, they are taken equal to $\langle 2s2s | 1/r_{1,2} | 2s2s \rangle$ or $\langle 1s2s | 1/r_{1,2} | 1s2s \rangle$ integrals. Therefore they are independent of the chosen mode.

In the electronic reaction butadiene \rightarrow cyclobutene, the main stereospecific correction appears to come from the second order $\pi \rightarrow \pi^*$ delocalization effects. If one does not use the CNDO approximations for the bielectronic integrals, some diexcitations with a $\pi \rightarrow \pi^*$ charge transfer would lead to stereospecific effects; the $(\varphi_k \rightarrow \varphi_k^*, \varphi_1 \rightarrow \varphi_2^*)$ diexcited states interact with Φ_0 by an integral of the form $\langle \varphi_1 \varphi_k | \varphi_2^* \varphi_k^* \rangle$. When developed by the Mulliken approximation, this integral is still proportional to the overlap $\langle \varphi_1 | \varphi_2^* \rangle$ and therefore larger in the conrotatory mode than in the disrotatory one.

(b) Distorted Final State Representation. One can consider the same geometry as in the preceding case and the same hybridization of the atomic orbitals. The only change concerns the definition of the molecular orbitals on these atomic orbitals according to eq 4. One may notice that in this case the bond MO's are also symmetry MO's. Let us consider the delocalization correction arising from the electron jump $\varphi_1 \rightarrow \varphi_2^*$. φ_1 is symmetrical with respect to the symmetry plane kept along the disrotatory mode while in this mode φ_2^* is antisymmetrical. Thus $\langle \varphi_1 | h | \varphi_2^* \rangle$ is zero in the disrotatory mode. On the contrary φ_1 and φ_2^* are both antisymmetrical with respect to the axis of symmetry

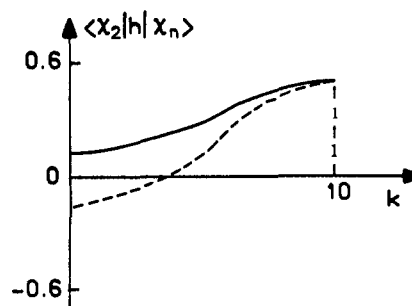


Figure 3. Evolution of the overlap $\langle \chi_2 | h | \chi_n \rangle$ between the terminal π atomic orbitals along the reaction path for the two modes: solid lines denote the disrotatory mode, dotted lines the conrotatory mode.

kept along the conrotatory mode, and one gets a non-zero delocalization stabilization in this mode.

$$\frac{\langle \varphi_1 | h | \varphi_2^* \rangle_c^2}{\Delta E_{\varphi_1 \rightarrow \varphi_2^*}} < 0 \quad \frac{\langle \varphi_1 | h | \varphi_2^* \rangle_d^2}{\Delta E_{\varphi_1 \rightarrow \varphi_2^*}} = 0 \quad (17)$$

The same conclusions holds for the inverse delocalization $\varphi_2 \rightarrow \varphi_1^*$. Again the delocalization between the reacting MO's favors the conrotatory mode.

(c) Biradical Representation. Again, for the same geometry and for the same definition of the hybrid atomic orbitals, the zero-order wave function is taken as

$$\Phi_0 = | \dots \varphi_1 \bar{\varphi}_1 (\chi_1 \bar{\chi}_4 \pm \chi_4 \bar{\chi}_1) | \quad (18)$$

with

$$\varphi_1 = (\chi_2 + \chi_3) / \sqrt{2} \quad (19)$$

At the second order, one has to consider the delocalization excitations $\chi_1 \rightarrow \chi_4$ and $\chi_4 \rightarrow \chi_1$ for which neither the sign nor the order of magnitude change, $\chi_1 \rightarrow \varphi_1^*$ and $\varphi_1 \rightarrow \chi_1$ which are equal in the two modes, and $\chi_4 \rightarrow \varphi_1^*$ and $\varphi_1 \rightarrow \chi_4$, the sign of which changes with the mode. But, in the second order, these interactions occurring in squared matrix elements do not give a difference between the two modes.

One has to go the third order to find stereospecific interactions by a circular process. The interaction between singly excited states, for instance, $\chi_1 \rightarrow \chi_4$ and $\varphi_1 \rightarrow \chi_4$

$$\langle \Phi_0 | H | \Phi_{\chi_1 \rightarrow \chi_4} \rangle \langle \Phi_{\chi_1 \rightarrow \chi_4} | H | \Phi_{\varphi_1 \rightarrow \chi_4} \rangle \langle \Phi_{\varphi_1 \rightarrow \chi_4} | H | \Phi_0 \rangle \times (\Delta E_{\chi_1 \rightarrow \chi_4}) (\Delta E_{\varphi_1 \rightarrow \chi_4})$$

gives the contribution

$$-\langle \chi_1 | h | \chi_4 \rangle \langle \varphi_1 | h | \chi_1 \rangle \langle \chi_4 | h | \varphi_1 \rangle / \Delta E^2 \quad (20)$$

As is apparent from Figure 1, $\langle \chi_1 | h | \chi_4 \rangle$ and $\langle \varphi_1 | h | \chi_1 \rangle$ are always negative, while $\langle \chi_4 | h | \varphi_1 \rangle \simeq 1/\sqrt{2} \langle \chi_4 | h | \chi_3 \rangle$ is negative in the disrotatory mode, positive in the conrotatory mode.

In the biradical representation, the first stereospecific interaction terms appear at the third order for two double bonds, while it occurred in the second-order corrections for the closed shell zero-order wave function. But one finds the same qualitative results, which are therefore independent on the choice of the fully localized zero-order wave function.

(4) Photochemical Reaction. For the photochemical reactions, one has to consider an excited state Φ_0^* . This state can no longer be represented by a

single determinant since the possible local excitations between the localized molecular orbitals lead to determinants which are not eigenfunctions of the symmetry operators of the system and which are degenerate between themselves. One must represent the excited states as linear combinations of several determinants representing different local excitations. For instance, for the butadiene molecule

$$\Phi_0^* = \alpha | \dots (\varphi_1 \bar{\varphi}_1^* \pm \varphi_1^* \bar{\varphi}_1) \varphi_2 \bar{\varphi}_2 | + \alpha' | \dots \varphi_1 \bar{\varphi}_1 (\varphi_2 \bar{\varphi}_2^* \pm \varphi_2^* \bar{\varphi}_2) | + \beta | \dots (\varphi_1 \bar{\varphi}_2^* \pm \varphi_2^* \bar{\varphi}_1) \varphi_2 \bar{\varphi}_2 | + \beta' | \dots \varphi_1 \bar{\varphi}_1 (\varphi_2 \bar{\varphi}_1^* \pm \varphi_1^* \bar{\varphi}_2) | \quad (21)$$

One obtains the coefficients α , α' , β , and β' and the energy of Φ_0 by diagonalizing an excitonic configuration interaction matrix²¹ built between the various excited fully localized determinants. In the butadiene case, this excitonic matrix presents the following form

$\Phi_{1 \rightarrow 1^*}$	$\Phi_{2 \rightarrow 2^*}$	$\Phi_{1 \rightarrow 2^*}$	$\Phi_{2 \rightarrow 1^*}$
E	b_{12}	$\beta_{1^* 2^*}$	$-\beta_{12}$
	E	$-\beta_{12}$	$\beta_{1^* 2^*}$
		E'	0
			E'

where

$$\begin{aligned} b_{12} &= \langle \varphi_1 \varphi_2^* | 1/r_{1,2} | \varphi_1^* \varphi_2^* \rangle \\ \beta_{1^* 2^*} &= \langle \varphi_1^* | h | \varphi_2 \rangle \\ \beta_{12} &= \langle \varphi_1 | h | \varphi_2 \rangle \end{aligned} \quad (22)$$

The b_{12} integral is independent of the mode while the integrals $\beta_{1^* 2^*} = -\beta_{12} = (+\langle \chi_1 | h | \chi_4 \rangle - \langle \chi_2 | h | \chi_3 \rangle)/2$, according to the conrotatory or disrotatory character of the mode. So these two integrals are more important when the mode is disrotatory. It follows that the lowest eigenvalue of the matrix is lower, which favors the disrotatory mode of butadiene cyclization.

In the final state representation (cyclobutene), an analogous treatment may be built implying the π and the σ bonds and again the integrals $\beta_{1^* 2^*}$ and $-\beta_{12}$ are larger in the disrotatory mode and zero in the conrotatory mode, as seen from eq 4 and Figure 1, favoring the disrotatory mode. One also may consider that in the distorted cyclobutene, the excitation is kept on the π bond φ_1 ; then the interaction of the singly excited $\pi-\pi^*$ state $\varphi_1 \rightarrow \varphi_1^*$ with the singly excited state $\varphi_1 \rightarrow \varphi_2^*$ leads to a second-order stabilization $\langle \varphi_1^* | h | \varphi_2^* \rangle^2 / \epsilon_1 - \epsilon_2$. In the conrotatory mode this correction is zero, due to the symmetry of the MO's, while it is important in the disrotatory mode. A similar demonstration is feasible in the biradical representation for the third-order correction.

III. Numerical Study of the Butadiene-Cyclobutene Reaction Using Localized MO's. Geometries. We have chosen for the initial and final configurations the butadiene and cyclobutene geometries given in the literature^{22, 23} except for the fact that we used the same CH

(21) W. T. Simpson, *J. Amer. Chem. Soc.*, **73**, 5363 (1951); **77**, 6164 (1955).

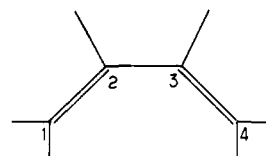
(22) A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1967); A. R. H. Cole, G. M. Moroy, and G. A. Osborne, *Spectrochim. Acta*, **23**, 909 (1967).

(23) E. Elihu Goldish, K. Hedberg, and V. Schomaker, *J. Amer. Chem. Soc.*, **78**, 2714 (1956).

bond lengths for the two molecules. The reaction path is determined by nine intermediate geometries where all angles α_j and bond distances ρ_i are modified in the same ratio with respect to the total change ($\Delta\alpha_i$, $\Delta\rho_i$) between the initial and final conformations

$$\frac{d\rho_i}{\Delta\rho_i} = \frac{d\alpha_j}{\Delta\alpha_j} = \frac{k}{10} \quad k = 0-10$$

In such a reaction path, all the bond, dihedral angles, and bond lengths vary in the same way. This hypothesis is not compulsory but it allows the construction of a likely reaction path with a small amount of calculations. In a later paper, several of these degrees of freedom will be varied independently. In a preliminary study we varied independently the distance between C₁ and C₄ (in fact the bond distance C₂C₃ and the bond angles C₁C₂C₃ and C₂C₃C₄) on one hand, and the torsional process around the C₁C₂ and C₃C₄ bonds on the other hand (in fact the bond and dihedral angles relative to the CH bonds, and the C₁C₂ and C₃C₄ bond lengths). The preferred path appeared to occur for an equal variation of these two categories of degrees of freedom. Therefore we shall only give the curves relative to the simple reaction paths.



Fully Localized Zero-Order Representations. From $k = 0$ to 6, we have built and perturbed the determinant constructed from the fully localized molecular orbitals of the butadiene system.

From $k = 4$ to 10, we have built and perturbed the determinant constructed from the fully localized MO's of the cyclobutene molecule. Therefore in the presumed region of the transition state ($k = 4-6$) we have two competitive representations. For this region too, we also studied the biradical representation. In all these representations the MO's are built with two hybrid orbitals obtained by the Del Re's maximum overlap criterion.¹⁸ However, the four atomic orbitals which enter the two π MO's destroyed in the reaction are determined by orthogonality to the other σ atomic orbitals.²⁴ This process gives the same set of AO's for a given k in the three representations. The only difference between these three representations concerns the π MO's constructed with the four AO's resulting from the orthogonalization to the σ AO's. This is in conformity with the PCILO algorithm.^{14e}

One can expect that the butadiene representation becomes worse when one comes close to the cyclobutene conformation, *i.e.*, for large k . Reciprocally, the cyclobutene representation should be bad for small k . One may therefore expect that the energy curves of the two representations intersect somewhere in the transition state region. One can choose for the corresponding values of k the representation which gives the lower energy. The reaction path energy curve will appear then as a hill with an angular top. In fact, for the transition state region, it may occur that none of the representations is reasonable enough to give a good convergence

(24) In fact these two main MO's are one π and one σ MO in the cyclobutene representation.

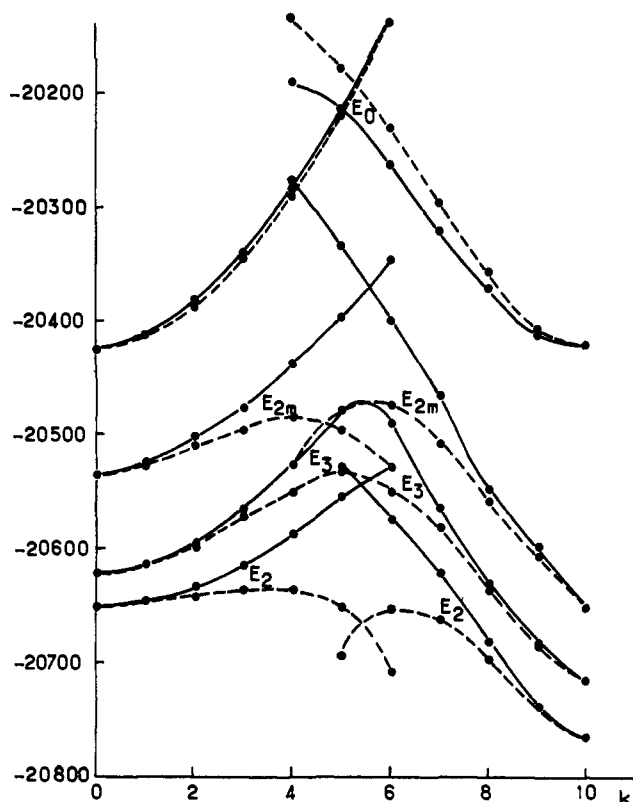


Figure 4. Ground-state energies in kcal/mol as a function of k . For this figure and for Figures 5 and 6, the solid lines represent the conrotatory mode. E_0 represents the zero-order energy, E_{2m} represents the energy corrected to the second order by the monoexcited states, E_2 represents the energy including the full second-order correction, and E_3 represents the energy corrected to the third order.

of the perturbation series. In such a case one can smooth the curves by an approximate interpolation, but for further calculations one should make some configuration interaction before the perturbation development, the zero-order wave function becoming then a linear combination of several determinants.

We have used in this calculation the Pople and Segal CNDO/2 parametrization.²⁰

Zero-Order Energy. The zero-order energy (including the nuclear repulsion) gives a very high barrier for the two modes: 230 kcal/mol for the conrotatory mode (from the butadiene) and 210 kcal/mol for the disrotatory mode (see E_0 in Figure 4). Contrary to the experimental result, the disrotatory mode is favored by 20 kcal/mol but this difference is weak. In the two modes the relative interatomic distances (especially between the terminal H atoms) are completely different for a given k . One might fear that large energy differences occur between the two modes due to differences in the short-range repulsion energies. Actually a compensation occurs between the differences of the nuclear repulsion energies and the differences of the electronic energies; it appears that the nuclear repulsion energy would favor the conrotatory mode by about 50 kcal/mol.

Therefore the assumption made in section II that the zero-order energies of the two modes are similar appears to be reasonable.

At that stage, the butadiene is more stable than the cyclobutene by 10 kcal/mol (the experimental value being 20 kcal/mol²⁵).

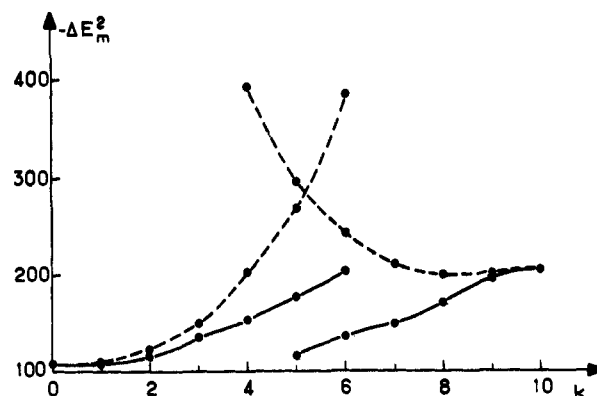


Figure 5. Second-order delocalization energy correction (in kcal/mol) as a function of k .

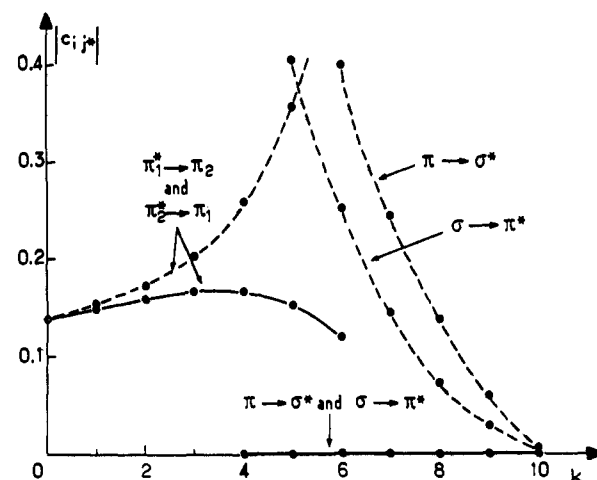


Figure 6. Absolute value of the coefficients of the main charge transfer states ($\pi_1 \rightarrow \pi_2^*$ and $\pi_2 \rightarrow \pi_1^*$ (in butadiene) and $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ (in cyclobutene)) as a function of k : π_1 and π_2 are the two π bonds of butadiene, π is the π bond of cyclobutene, and σ is the cyclobutene CC bond which is broken in the reaction.

Second-Order Energy. From the demonstration given in section II, the preference of the conrotatory mode should be due to the effect of the $\pi\pi^*$ delocalization monoexcited states. E_{2m} (Figure 4) shows that the monoexcitations actually bring the curve of the conrotatory mode to culminate at 110 kcal/mol under the top of the hill for the disrotatory mode. The butadiene and cyclobutene representations are in complete agreement. The activation energy is about 55 kcal/mol for the conrotatory mode when starting from the butadiene molecule, and occurs for $k = 5-6$. The cyclobutene molecule appears to be more stable than the butadiene molecule by about 115 kcal/mol.

In these nonpolar molecules, the polarization corrections are weak and nonstereospecific. The evolution of the second-order delocalization corrections (Figure 5) shows the dominant role of the charge transfer monoexcitations $i \rightarrow j^*$.

In order to analyze the respective role of the σ unchanged MO's and of the π MO's which are destroyed in the reaction, we have given in Figure 6 the evolution of the main first-order coefficients of the charge transfer

(25) W. G. Dauben, 13th Chemistry Conference of the Solvay Institute, "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N. Y., 1967, p 171.

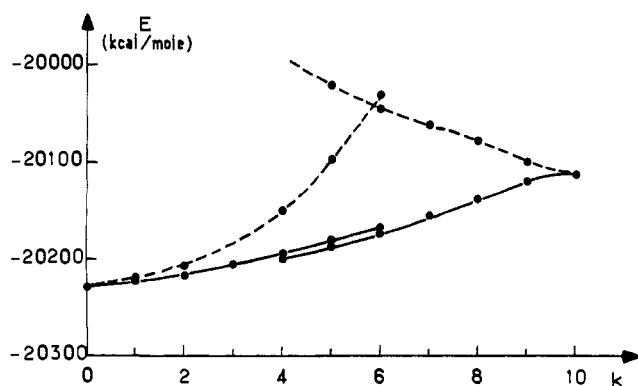


Figure 7. Energy (in kcal/mol) of the lowest singlet excited state after an excitonic treatment.

monoexcitations. The most important coefficients are those predicted in section II, *i.e.*, those of the $\pi \rightarrow \pi^*$ charge transfer states which increase much more in the conrotatory mode than in the disrotatory one. (They even are zero for the disrotatory mode of the cyclobutene molecule, due to cancellations between atomic integrals.) A detailed analysis of the results indicates that there exists some stereospecific $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ charge transfers; for instance in the cyclobutenic representation, for $k = 5$ the excitations from the terminal CH bonds toward the σ CC bond which is going to be broken are respectively 0.15 and 0.075 for the conrotatory and the disrotatory modes. But the order of magnitude of these coefficients and their stereospecificity is much smaller than those of the $\pi \rightarrow \pi^*$ delocalization states.

The diexcitations are not supposed to give stereospecific contributions. The two bonds diexcitations ($i \rightarrow i^*$ and $j \rightarrow j^*$) which are responsible for the intramolecular dispersion forces only favor the conrotatory mode by 2 kcal/mol in the transition state region. The intrabond correlation correction, due to the diexcitations in the same bond, also favors the conrotatory mode by 6 kcal/mol in the cyclobutene representation for $k = 6$. This difference is not easy to interpret, but it remains small when compared to the stereospecific corrections of the monoexcitations. This explains the fact that the total second-order correction gives an energy curve (E_2 , Figure 4) rather similar to that obtained from the monoexcitations second-order effects (E_{2m} , Figure 4) with an interpolated energy differences in the activation energies of the two modes of about 95 kcal/mol.

The activation energy from the butadiene molecule is about 20 kcal/mol for the conrotatory mode, but the energy of the final state is much too small under the energy of the initial state. This is not due to the perturbative method, but to the CNDO/2 parametrization which fails to reproduce the relative stabilities of various isomers when some of them involve strained cycles;²⁶ the SCF-CNDO calculations also give a cyclobutene much more stable than the butadiene molecule.²⁷

For E_2 in the Figure 4, one may notice a potential hole in the transition state region ($k = 5-6$) for the conrotatory mode. One cannot give to this hole the physical signification of a stable activated complex;

(26) F. Jordan, M. Gilbert, J. P. Malrieu, and U. Pincelli, *Theor. Chim. Acta*, **15**, 211 (1969).

(27) Hoarau, to be submitted for publication.

it comes from the increasing divergence of the perturbation process for the conrotatory mode (especially the intrabond diexcitation correction in the broken σ bond of the cyclobutene).

Third-Order Results. F_3 (Figure 4) gives the total energy after the third-order corrections. These curves given in Figure 4 result from an interpolation between $k = 5$ and 6 for the disrotatory mode and between $k = 6$ and 7 for the conrotatory; in these intervals the cyclobutene representation diverges (due to the intrabond diexcitations in the broken σ bond). The conrotatory is still favored but the activation energy from the butadiene is now about 60 kcal/mol from the butadiene for the conrotatory mode and the difference between the heights of the hills is 65 kcal/mol.

Two third-order contributions appear to be stereospecific, the interaction between the monoexcited delocalization states ($i \rightarrow j^*$ with $i \rightarrow k^*$ and $k \rightarrow j^*$) and the interaction between delocalization monoexcited states ($i \rightarrow j^*$) with the two bond diexcitations ($i \rightarrow i^*$ and $j \rightarrow j^*$). The first one disfavors the conrotatory mode by 35 kcal/mol and the second one favors it by 20 kcal/mol.

The first contribution necessarily involves σ MO's (since there are only two π MO's); if i and j are the two π MO's, k may be the σ MO of the central CC simple bond, and the analysis of this contribution is similar to that made below for the hexatriene molecule. The third-order effects cannot reverse the results obtained from the second-order corrections.

Biradical Representation. The zero-order energy of the biradical representation is much higher than those of the final and initial state representations except for $k = 5$. For that geometry, the results (see Table I)

Table I. Energy Results for the Biradical Representation of the Transition State ($k = 5$, in kcal/mol)

	Conrotatory mode	Disrotatory mode
Zero order	-20,221	-20,218
Second-order effect of the monoexcited states	-178	-185
Second-order corrected energy	-20,497	-20,502
Third-order effect of the interaction between the monoexcited states	31	50
Third-order corrected energy	-20,466	-20,451

show that (a) the zero-order result favors the conrotatory mode by only 4 kcal/mol, (b) the disrotatory mode is favored by 5 kcal/mol after the second-order result, (c) the stereospecificity is actually obtained after the third-order corrections, as expected from the theoretical demonstration in section II: the conrotatory mode is favored by 15 kcal/mol. This is due to the interaction between the delocalization monoexcitations which give respectively 50 and 31 kcal/mol corrections.

Stereospecificity of the Photochemical Reaction. Figure 7 reports the energy curves in the lowest excited state. The energy is obtained after an excitonic treatment, representing the configuration interaction between the local $\pi \rightarrow \pi^*$ monoexcited states. The form of this excitonic CI matrix has been given in section II.

The excitation energies are too high (9 eV for the butadiene instead of 5.7 eV, and 13.6 eV for the cyclo-

butene instead of 7.2 eV); this is due to the use of the CNDO parameters but the stereospecificity is well reproduced. The curves do not cross for the disrotatory mode, but they are very close to each other and no barrier occurs in this mode, which is the favored mode in the excited state (in agreement with the experimental result). Our calculation does not confirm the origin of the stereoselectivity in the photochemical reaction suggested by a π valence bond calculation.²⁸ According to this work, in the disrotatory mode the symmetrical excited state energy surface crosses the surface of the antisymmetrical excited states and presents a well for intermediate configurations. The geometry changes leaving the twofold symmetry allowed passage from the antisymmetrical excited state to this well, and a non-radiative deexcitation occurs toward the ground state. In our calculation, the symmetrical state never crosses the antisymmetrical one. This difference may be due either to the differences between the parametrizations of Pariser-Parr used in ref 27 and CNDO, or to differences between the geometry changes of the intermediate states.

Previous numerical extended Hückel calculations⁴ have questioned whether the stereospecificity was actually determined by the heights of the potential barriers relative to the different modes. Our more elaborate all-valence electron calculation confirms the existence of these qualitative differences in the characteristics of the potential surfaces and therefore substantiates the Woodward-Hoffmann demonstrations¹⁻² and other calculations.^{3, 28}

Taking into account the fact that we used an inadequate parametrization and that the perturbation series may diverge for the transition region, one cannot be surprised not to have a quantitative agreement with the experimental thermodynamic results.

Our purpose was mainly to verify the assumptions made in the localized demonstration of the stereospecificity given in section II. Actually we have checked that (a) there was no significant stereospecific difference in the energy of the fully localized determinant; (b) the second-order delocalization corrections are responsible for the stereospecificity and favor the experimentally preferred mode (the excitonic treatment also gives the experimental result for the excited state reaction); (c) the third-order correction shows the intervention of correlation effects and σ MO's. These effects are opposite to the second-order π delocalization effects, but they cannot reverse the conclusion. The hypothesis that the stereospecificity is determined by the lowest order stereospecific term appears to be reasonable. Moreover it is interesting to notice that the preferred mode is the same all along the reactional path; the two energetic curves do not cross. In such a case the analysis of the stereospecificity from the stabilization of the perturbed (or polarized) initial or final states is relevant.²⁹

IV. Extension of the Localized Demonstration to All Electrocyclic Reactions. The demonstration given in section II for two double bonds may be generalized to any number of double bonds, but the stereospecificity appears at higher and higher orders of the perturbation series, so that a simple technique is necessary to handle

(28) W. Th. A. M. Van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968).

(29) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin New York, N. Y., 1966, p 287.

the perturbation series. The many-body theory diagrammatic techniques provide such an instrument.

Brief Introduction of the Diagrammatic Conventions. One will represent by diagrams³⁰ the different terms of the perturbation series.

The first-order correction is zero, due to our H_0 definition. The second-order correction is given by

$$E^2 = \sum_{I \neq 0} \langle \Phi_0 | v | \Phi_I \rangle^2 / (E_0 - E_I) \quad (23)$$

with Φ_0 as the zero-order approximation for the wave function, and Φ_I as the excited states orthogonal to Φ_0 . All Φ_I are eigenfunctions of H_0 . E_0 and E_I represent the eigenvalues of H_0

$$H_0 \Phi_I = E_I \Phi_I \quad (24)$$

The third-order correction is given by

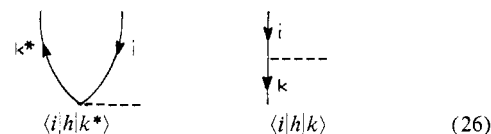
$$E^3 = \sum_I \sum_J \frac{\langle \Phi_0 | v | \Phi_I \rangle \langle \Phi_I | v | \Phi_J \rangle \langle \Phi_J | v | \Phi_0 \rangle}{(E_0 - E_I)(E_0 - E_J)} \quad (25)$$

In such a contribution we represent the contributions of the various sets of states ($\Phi_I, \Phi_J, \Phi_K, \dots$) by diagrams which give at once the set of states $\Phi_I, \Phi_J, \Phi_K, \dots$ and successive matrix elements $\langle \Phi_0 | v | \Phi_I \rangle, \langle \Phi_I | v | \Phi_J \rangle$, etc. Each excited state Φ_I is represented by a set of vertical propagation lines, each of them being characterized by the index of one of the occupied or virtual molecular orbitals implied in the excitation process from Φ_0 toward Φ_I . The downward lines symbolize the holes of Φ_I (i.e., the levels which are occupied in Φ_0 and empty in Φ_I), and the upward lines symbolize the particles of Φ_I (i.e., the levels which are empty in Φ_0 and occupied in Φ_I). For instance, the following set of propagation lines

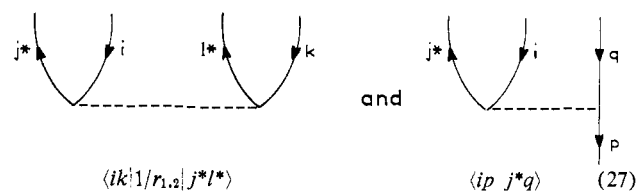


represents the triexcited state obtained by replacing in $\Phi_0 \varphi_i$ by φ_{k^*} , φ_j by φ_{i^*} , and φ_p by φ_{q^*} .

The matrix elements $\langle \Phi_I | H | \Phi_J \rangle$ are visualized by dotted horizontal interaction lines. The elements of the mono-electronic operator bear only one node, on which a propagation line comes and from which a propagation line departs. For instance



The bielectronic matrix elements bear two nodes. Each of these nodes is again the departure and arrival point of a propagation line. Each node represents an electronic distribution. For instance



or more briefly $\langle ik | j^* i^* \rangle$.

(30) For a systematic introduction of the diagrams of the many body problem see, for instance, N. H. March, W. H. Young, and S. Sampanthar, "The Many Body Problem in Quantum Mechanics," Cambridge University Press, London, 1968.

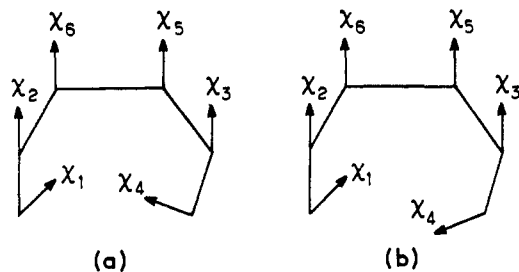
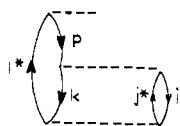


Figure 8. Definition of the atomic orbitals for the intermediate states in the hexatriene \rightarrow cyclohexadiene reaction. Same comments as in Figure 2.

A diagram for a n th order correction to the energy involves n successive interaction lines and therefore n matrix elements, and $(n - 1)$ denominators equal to the zero-order excitation energies $(E_0 - E_I)$ toward the successive excited states Φ_I which one reads from the propagation lines between two successive interaction lines.³¹ For instance, the third-order diagram



may be read as

$$\frac{\langle ik|j^*l^*\rangle\langle j^*p|ik\rangle\langle l^*|h|p\rangle}{(E_0 - E(j^* \ l^*)) (E_0 - E(l^* \ p))}$$

Hexatriene \rightleftharpoons Cyclohexadiene Reaction $n = 3$. If we assume the definition of the AO's given in Figure 8, the bonding orbitals will be in the initial state representation

$$\begin{aligned} \varphi_1 &= (\chi_2 + \chi_1)/\sqrt{2} \\ \varphi_2 &= (\chi_3 \pm \chi_4)/\sqrt{2} \\ \varphi_3 &= (\chi_5 + \chi_6)/\sqrt{2} \end{aligned} \quad (28)$$

according to the disrotatory or conrotatory character of the mode. The related antibonding MO's are obtained by changing the sign of the first AO in these expressions.

As we have seen in the $n = 2$ reaction that the lowest order stereospecific corrections are more important than the higher order ones, we shall assume later on that the stereospecificity is determined by the lowest order stereospecific correction.

We make here a *further hypothesis*: the monoelectronic integrals between the AO's which are not bonded, neither in the initial nor in the final state, are neglected. The overlap between these AO's is actually about five times smaller than the overlap between the AO's which are linked or will be linked in the course of the reaction. Therefore the integrals $\langle \chi_1|h|\chi_5 \rangle$, $\langle \chi_1|h|\chi_6 \rangle$, $\langle \chi_1|h|\chi_3 \rangle$, $\langle \chi_2|h|\chi_6 \rangle$, etc., will be neglected.

It results from Figure 8 and eq 28 that the integrals $\langle \varphi_1|h|\varphi_2 \rangle$, $\langle \varphi_1|h|\varphi_2^* \rangle$, $\langle \varphi_1^*|h|\varphi_2 \rangle$, and $\langle \varphi_1^*|h|\varphi_2^* \rangle$ are all equal to $\mp \langle \chi_1|h|\chi_4 \rangle$ according to the con- or disrotatory character of the reaction, and therefore positive in the conrotatory mode and negative in the disrotatory one.

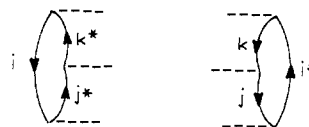
(31) These conventions are not sufficient to build the perturbation series, but they allow the reading of the diagrams which are introduced hereafter in the demonstration.

The other π monoelectronic molecular integrals are not stereospecific. The second-order delocalization correction are not stereospecific since the integrals are squared.

It is necessary to analyze the third-order corrections to find a stereospecific correction. The stereospecific corrections will come from the interaction between delocalization monoexcited configurations; in the CNDO hypothesis, this term is reduced^{14e} to

$$4 \sum_i \sum_j \sum_k \frac{\langle \varphi_i|h|\varphi_j^* \rangle \langle \varphi_j^*|h|\varphi_k^* \rangle \langle \varphi_k^*|h|\varphi_i \rangle}{(E_0 - E(j^* \ i)) (E_0 - E(k^* \ i))} - \frac{\langle \varphi_j|h|\varphi_i^* \rangle \langle \varphi_j|h|\varphi_k \rangle \langle \varphi_i^*|h|\varphi_k \rangle}{(E_0 - E(j^* \ i)) (E_0 - E(k^* \ i))} \quad (29)$$

These corrections correspond to the diagrams



In the hexatriene molecule one gets thus three combinations of indexes for the π correction

$$\begin{aligned} i = 1, & \quad j = 2, & \quad k = 3 \\ i = 2, & \quad j = 1, & \quad k = 3 \\ i = 3, & \quad j = 1, & \quad k = 2 \end{aligned}$$

Let us consider the first combination of indexes. (The other combinations give equal quantities.) The numerators of eq 29 will be equal to

$$\langle \varphi_1|h|\varphi_2^* \rangle \langle \varphi_2^*|h|\varphi_3^* \rangle \langle \varphi_3^*|h|\varphi_1 \rangle$$

and

$$-\langle \varphi_2|h|\varphi_1^* \rangle \langle \varphi_2|h|\varphi_3 \rangle \langle \varphi_1^*|h|\varphi_3 \rangle \quad (30)$$

Expressing these molecular integrals in terms of atomic integrals, one gets then a contribution

$$\pm 24 \langle \chi_1|h|\chi_4 \rangle \langle \chi_2|h|\chi_6 \rangle \langle \chi_3|h|\chi_3 \rangle / \Delta E^2$$

according to the disrotatory or conrotatory character of the cyclization. As the atomic integrals are negative, the disrotatory mode is favored. One might verify from eq 15-24 of ref 14e that in the CNDO hypotheses the other third-order corrections do not involve clearly stereospecific contributions. In the final state (cyclohexadiene) representation, referring to Figure 3, the bond MO's are one σ bond in course of being broken

$$\varphi_1 = (\chi_1 + \chi_4)/\sqrt{2} \quad (31)$$

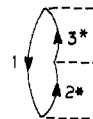
and two π bonds

$$\varphi_2 = (\chi_3 + \chi_6)/\sqrt{2}$$

$$\varphi_3 = (\chi_6 + \chi_2)/\sqrt{2}$$

The only change of sign between the two modes concerns the interactions between the bonds φ_1 and φ_2 as it appears clearly from the figure.

The demonstration is strictly the same as in the initial state representation. In the cyclohexadiene, for instance, the third-order diagram



gives the product $\langle \varphi_1 | h | \varphi_2^* \rangle \langle \varphi_2^* | h | \varphi_3^* \rangle \langle \varphi_3^* | h | \varphi_1 \rangle$. One obtains therefore a contribution

$$+\langle \chi_4 | h | \chi_3 \rangle \langle \chi_4 | h | \chi_5 \rangle \langle \chi_1 | h | \chi_2 \rangle / \Delta E^2 \quad (32)$$

which has the same sign as $\langle \chi_4 | h | \chi_3 \rangle$. Now $\langle \chi_4 | h | \chi_3 \rangle$ is negative in the disrotatory mode and positive in the conrotatory mode. Again, the disrotatory mode is favored.

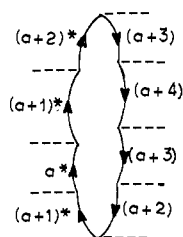
The same demonstration might be done for the biradical state representation (in this case the stereospecificity would arise from fourth-order diagrams). In any case the stereospecificity appears to be determined by circular delocalization interactions around the reacting cycle.

Generalization to n Double Bonds. The π atomic orbitals and the bond MO's of the n double bond polyene may be defined as in Figure 9 by inserting supplementary double bonds in the scheme of hexatriene. The MO's are defined according to

$$\begin{aligned} \varphi_1 &= (\chi_2 + \chi_1) / \sqrt{2} \\ \varphi_2 &= (\chi_3 + \chi_4) / \sqrt{2} \\ \varphi_3 &= (\chi_5 + \chi_6) / \sqrt{2} \\ \varphi_n &= (\chi_{2n-1} + \chi_{2n}) / \sqrt{2} \end{aligned} \quad (33)$$

Then the integrals $\langle \varphi_1 | h | \varphi_2 \rangle$, $\langle \varphi_1 | h | \varphi_2^* \rangle$, $\langle \varphi_2 | h | \varphi_1^* \rangle$, and $\langle \varphi_1^* | h | \varphi_2^* \rangle$ are all positive in the conrotatory mode and all negative in the disrotatory one, as we have seen for the hexatriene molecule. The other integrals are not stereospecific.

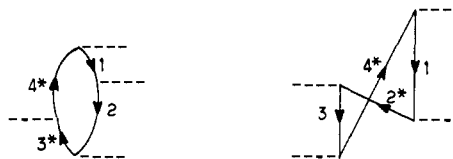
The second-order π - π^* delocalization diagrams give $2(n-1)$ contributions between adjacent bonds which are not qualitatively stereospecific. One may analyze the diagrams of order $3 \leq k < n$ which only imply mono-electronic interactions on their interaction lines. The diagrams which do not imply φ_1 (or φ_1^*) and φ_2 (or φ_2^*) are not stereospecific. The diagrams are negligible if they imply a long-range interaction between nonneighbor molecular orbitals. Therefore the non-zero diagrams of order $k < n$ imply a one-step progression along the chain from one bond a to the bond $l+a$, and then a regression to the point of departure by a one-step process, as occurs in the following diagram.



The nonzero diagrams implying only mono-electronic interactions are then necessarily of even orders. If they imply an interaction between the bonds 1 and 2 in the progression, another interaction between the bonds 2 and 1 appears in the return process: as the corresponding matrix elements are of the same sign for a given mode, these diagrams, even when they imply an interaction between the bonds 1 and 2, give the same correction for the two modes.

The stereospecific diagrams must imply an odd number of times for the interaction between the bonds 1 and 2

and they necessarily are of order $k \geq n$. If one considers the lowest order diagrams ($k = n$), which are supposed to be the dominant ones, one will get stereospecific contributions from the diagrams representing n interactions between the successive bonds of the chain in a cyclic process. For instance, for the octatetraene molecule, the diagrams

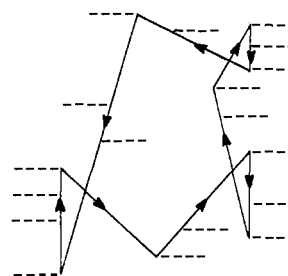


are stereospecific since the integrals $\langle \varphi_1 | h | \varphi_2 \rangle$ or $\langle \varphi_1 | h | \varphi_2^* \rangle$ which appear in these diagrams have opposite signs for the two modes.

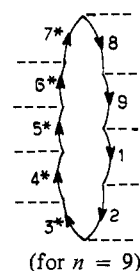
To demonstrate that the favored mode is conrotatory for an even number n of double bonds and disrotatory for an odd number n , one proceeds in the following manner.

(i) One first demonstrates that for a given mode and an n double bond polyene, all the n th-order diagrams which only imply mono-electronic interactions around the cycle have the same sign, whatever their topology and their indexation are.

In a full generality these diagrams look like the following diagram.



The $2v$ angular points correspond to the hole-particles interactions. There are $v-1$ crossing points of line which are of the same nature in the diagram. When $v = 1$ one has a "sausage" diagram implying only monoexcited intermediate states, like the diagram



Moreover there are p interactions on the upward lines (between particles) and q interactions on the downward lines (between holes) so that $p + q + 2v = n$. If one arranges the molecular orbitals in an increasing order along the cyclizing polyene, the interactions will take place between the MO's of successive bonds r and $r+1$.

The signs of the molecular orbitals coefficients may be chosen according to the following convention.

$$\begin{array}{cc} \frac{+ (r) +}{a} & \frac{+ (r+1) +}{a+1} \\ \frac{- (r^*) +}{(r^*)} & \frac{- (r+1)^* +}{(r+1)^*} \end{array}$$

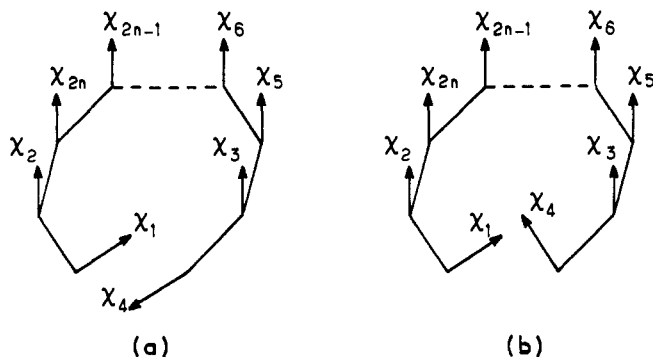


Figure 9. Definition of the atomic orbitals for the intermediate states of an n double bonds electrocyclic reaction. Same definition of (a) and (b) as in Figure 2.

The interactions between holes $\langle r|h|r+1 \rangle$ will be equal to $+p$ if $\beta = \langle \chi_a|h|\chi_{a+1} \rangle$. The interactions between particles will be equal to $-\beta$, and the interactions between holes and particles are given by

$$\begin{aligned}\langle r|h|(r+1)^* \rangle &= -\beta \\ \langle r^*|h|(r+1) \rangle &= +\beta\end{aligned}$$

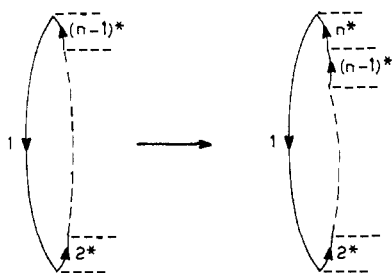
One can verify that if the diagram involves $2v$ angular points, there are v interactions $\langle r|h|(r+1)^* \rangle$ and v interactions $\langle r^*|h|(r+1) \rangle$.

Consequently, the product of the matrix elements occurring in the diagram has the sign $(-1)^{v+q}\beta^n$. The sign rules of the diagrams imply a sign change for each hole-hole interaction and for each crossing point of the upward lines (or downward lines) between themselves. So the diagram gives a contribution

$$\begin{aligned}(-1)^{v+q+p+v-1}\beta^n/\Delta E^{n-1} \\ (-1)^{n-1}\beta^n/\Delta E^{n-1}\end{aligned}$$

the sign of which depends on n only (for a given mode).

(ii) The sign of all these diagrams is obtained immediately from the consideration of a peculiar diagram, for instance, from the diagram representing the interaction between the various excited charge transfer states from the bond 1. One goes from such a diagram for the $(n-1)$ double bond polyenes to the corresponding diagram for n double bonds



by adding a supplementary interaction $\langle \varphi_{(n-1)^*}|h|\varphi_n^* \rangle$ and replacing the interaction $\langle \varphi_1|h|\varphi_{(n-1)^*} \rangle$ by $\langle \varphi_1|h|\varphi_n^* \rangle$. If the $(n-1)$ th-order diagram contribution is equal to $C \times \langle \varphi_{(n-1)^*}|h|\varphi_1 \rangle$, the contribution of the n th-order one is equal to

$$C \times \langle \varphi_{(n-1)^*}|h|\varphi_n^* \rangle \langle \varphi_n^*|h|\varphi_1 \rangle / \left(E_0 - E_1^{n^*} \right) \quad (34)$$

Now

$$\langle \varphi_{(n-1)^*}|h|\varphi_1 \rangle = \langle \varphi_n^*|h|\varphi_1 \rangle$$

and

$$\langle \varphi_{(n-1)^*}|h|\varphi_n^* \rangle = -\langle \chi_{1(n-1)}|h|\chi_{2n-1} \rangle$$

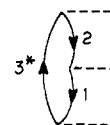
Therefore $\langle \varphi_{(n-1)^*}|h|\varphi_n^* \rangle$ is always positive while the denominator energy

$$E_0 - E_1^{n^*}$$

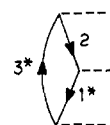
is always negative. The n th-order diagram contribution is therefore equal to the $(n-1)$ th-order contribution multiplied by a negative number and the preferred mode changes with the parity of the number of conjugated bonds implied in the reaction. As the preferred mode is conrotatory for $n=2$, the preferred mode is conrotatory for even n and disrotatory for odd n in agreement with the Woodward-Hoffmann rules.

The demonstration of the stereoselectivity rules for the excited state may be summarized as follows.

In the compounds with n double bonds ($n > 2$) the excitation is localized on the two terminal bonds which undergo a rotation.³² If one calls φ_1 and φ_2 the terminal molecular orbitals π which undergo a rotation, the zero-order wave function Φ_0 keeps the form of eq 21. Then the excitonic matrix reduced to the excited states built from φ_1 and φ_2 is no longer stereospecific since in $\beta_{1^*2^*}$ and β_{12} , $\langle \chi_i|h|\chi_j \rangle$ becomes negligible. The difference proceeds from $(n-1)$ th perturbation terms analogous to the stereospecific terms considered in the ground state, but where, henceforth, the molecular orbital 1^* , partially occupied in the Φ_0 state, becomes a hole and the molecular orbital 1, partially empty in Φ_0 , becomes a particle. For instance, for hexatriene besides the diagrams



one gets diagrams



These last diagrams give more important contributions than the first one because the associated denominators are much weaker (since they are differences between energies of monoexcited configurations) and with signs which are opposite to the first diagram signs, because the passage from φ_1 to φ_1^* reverses the sign of the matrix elements between φ_1 and φ_3 or between φ_1 and φ_2 . This results in an inversion of the favored cyclization mode in the excited state with the respect to the preferred one in the ground state.

Conclusion

The present localized demonstration of Woodward-Hoffmann rules for electrocyclic reactions requires

(32) J. Langlet, to be submitted for publication.

some hypotheses (about the atomic integrals) which are not necessary in the well-known demonstration based on correlation diagrams. However the Woodward-Hoffmann demonstration also required some energetical hypotheses (quasi-linearity of the variation of determinant energies and smallness of the interaction terms between determinants) which are as drastic as ours.

Taking into account from its very basis the spatial localization of the MO's, our method is not subject to the ambiguities of the correlation diagrams that we noticed on the cyclooctatetraene \rightarrow cubane reaction or the $(6 + 2)$ Diels-Alder reaction. Using localized MO's, the method works with the minimal number of MO's on the reacting circle without requiring the partial preliminary relocation which should in principle be necessary for the application of the basic correlation diagrams to substituted compounds.

In our demonstration the stereospecificity appears directly determined by the parity of the number of reacting bonds, without any symmetry consideration. The stereospecificity of the cyclization of the n bond polyenic chain results from n th-order corrections representing circular delocalization effects along the reacting circle; the sign of these contributions changes with the mode and the parity of n . It is amazing to notice at this point that an isomorphism definitely exists between this quantum chemical picture and the traditional dot-and-arrows intuitive chemical visualization of the chemical reaction. For instance, in the stereospecific diagram for $n = 3$, an electron jumps from bond 3 to the antibonding MO on bond 1, then an electron jumps from bond 3 to the vacant bonding MO on bond 2, and the electron in the antibonding MO φ_1^* on bond 1



turns back on bond 3 to occupy the vacant MO. The specificity of the quantum description lies in the knowledge of the nodal structure of bonding and antibonding MO's. (This is true in both the Woodward-Hoffmann demonstration and in this localized one.)

One interesting consequence of our demonstration is that the energy difference for the transition state of the two modes appearing at higher orders of the perturbation development, should tend to zero when the dimension of the reacting circle increases. If one does not neglect the mono-electronic integrals between nonbonded atoms, some lower order terms may balance the stereospecific n th-order contribution which should in principle be dominant. The experimentally known examples in fact only concern a few number of double bonds ($n = 3$). This demonstration suggests that for large enough n , the two nodes might compete with almost equal weights.

The PCILO-CNDO numerical calculation, although it does not give a quantitative agreement with experiment (due to the parametrization), confirms both the experimental results and the theoretical analysis. It will be completed in the near future by analogous *ab initio* PCILO calculations for $n = 2$ and other PCILO-CNDO calculations for $n = 3$.

The same type of demonstration applies with minor changes to the other types of concerted reactions. The corresponding demonstrations and numerical calculations will be given later.